1953

A petrographic and chemical study of the Bevier coal seam

Philip John Clarke

A PETROGRAPHIC AND CHEMICAL STUDY OF THE BEVIER COAL SEAM

BY

PHILIP JOHN CLARKE

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE, GEOLOGY MAJOR

Rolla, Missouri

1953

Approved by - Ray E. Morgan

Associate Professor of Economic Geology

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Samples of coal were taken at three inch intervals vertically down the Bevier seam at three localities in Macon and Randolph Counties. Channel samples were collected at the three localities. All samples were analyzed for ash content, total sulphur content, crucible swelling number, and volatile content. The channel samples were analyzed for "pyritic" sulphur, "sulphate" sulphur, and "organic" sulphur. Thin sections of the samples were used in an estimation of anthraxylon and attritus contents.

In all the samples studied, volatile content of the coal seemed to be related to the ash content and the sulphur content. Crucible swelling number also seemed to be related to the volatile content. No correlation was found between the petrographic properties (as seen in thin section) and the analysis figures for ash, sulphur, crucible swelling number, and volatile matter.

No apparent stratigraphic correlation could be made from one locality to another on the basis of detailed analysis. However, the rank of the coal is the same, and the shale bench is present in each locality. The lowest sulphur content found in any of the detailed samples was just over 2.0 per cent, a value which is referred to as the "background" sulphur. Of 64 analyses for sulphur, 31 samples contained between 2.0 and 2.5 per cent sulphur.

The coal ash contained a maximum of 0.01 per cent of germanium.

INTRODUCTION

A detailed study of the Bevier coal seam was made, with the object of correlating the petrographic properties with the properties of ash content, sulphur content, crucible swelling number, and volatile content of the samples studied. Samples were collected from three localities in Macon and Randolph Counties. The samples were taken at three inch intervals vertically through the seam, and examined in the laboratory for ash content, sulphur content, volatile content, coking quality, and in thin section for the relative proportions of the petrographic constituents. Channel samples were taken at the three localities, and analysed for ash content, sulphur content, volatile content, calorific value, and germanium concentration in the ash. Using these analysis figures, studies were made to find if there were correlations between the various properties.

The lithology of the seam was studied with a view to employing it in detailed correlation. Collecting localities 2 and 3 are separated by 500 yards. Locality 1 is eight miles to the north of locality 3. The position of these localities presents an opportunity to study local and medium distance correlation.

Germanium concentrations in the ash of the three channel samples were determined by a spectrographic method. This was a preliminary investigation to find if the coal could be used as a source of germanium.

Acknowledgements. Dr. O. R. Grawe and Prof. R. E.

Morgan of the Missouri School of Mines and Metallurgy, and Dr. E. L. Clark and Dr. W. V. Searight of the Missouri Geological Survey all made suggestions leading to the selection of this thesis topic. Professor Morgan introduced me to the collecting area, suggested methods for the collection of oriented specimens, and served as faculty supervisor and chairman of my Graduate Faculty Committee. He made many suggestions relating to problems of investigation and methods of attack.

Dr. R. M. Kosanke of the Illinois Geological Survey gave invaluable advice concerning coal petrology and thin section techniques. Dr. D. L. Frizzell of the Missouri School of Mines gave much constructive information during the working of the thesis. Mr. W. B. Howe of the Missouri Geological Survey gave advice in the preparation of the columnar section of the rocks in Macon and Randolph Counties.

Professor Morgan critically read the manuscript, and gave valuable advice on important revisions.

GEOLOGY OF THE BEVIER SEAM

In Macon and Randolph Counties, Missouri, the Bevier seam lies about 100 feet above the base of the Cherokee group in the Desmoinesian series of the Pennsylvanian system. The age of the Bevier coal is approximately equivalent to the Upper Staffordian beds of the Coal Measures (Upper Carboniferous) of Great Britain. Figure 2 shows a columnar section of the uppermost Cherokee rocks exposed in Macon and Randolph Counties.

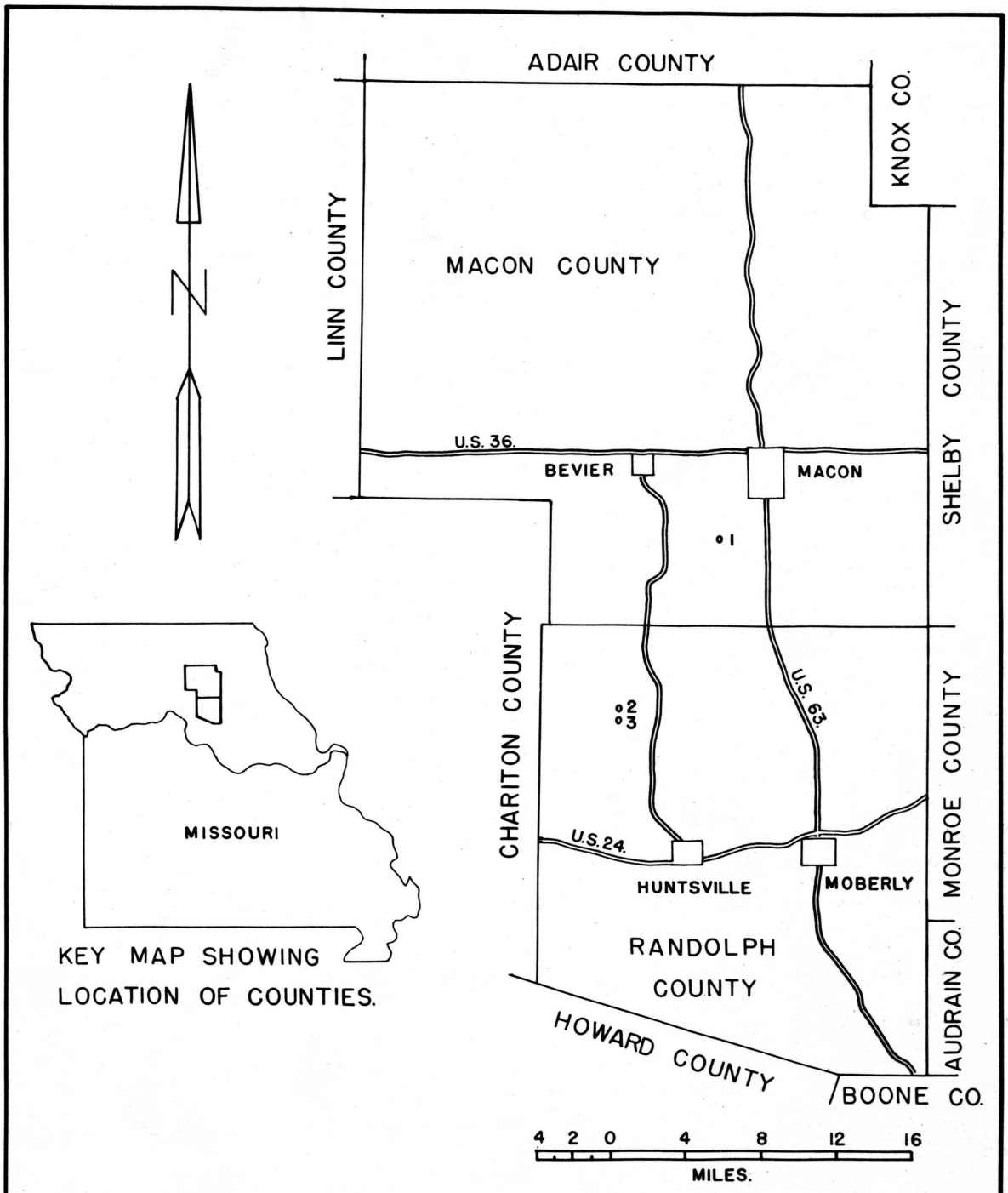


FIG. 1. MAP SHOWING COLLECTING LOCALITIES IN MACON AND RANDOLPH COUNTIES.

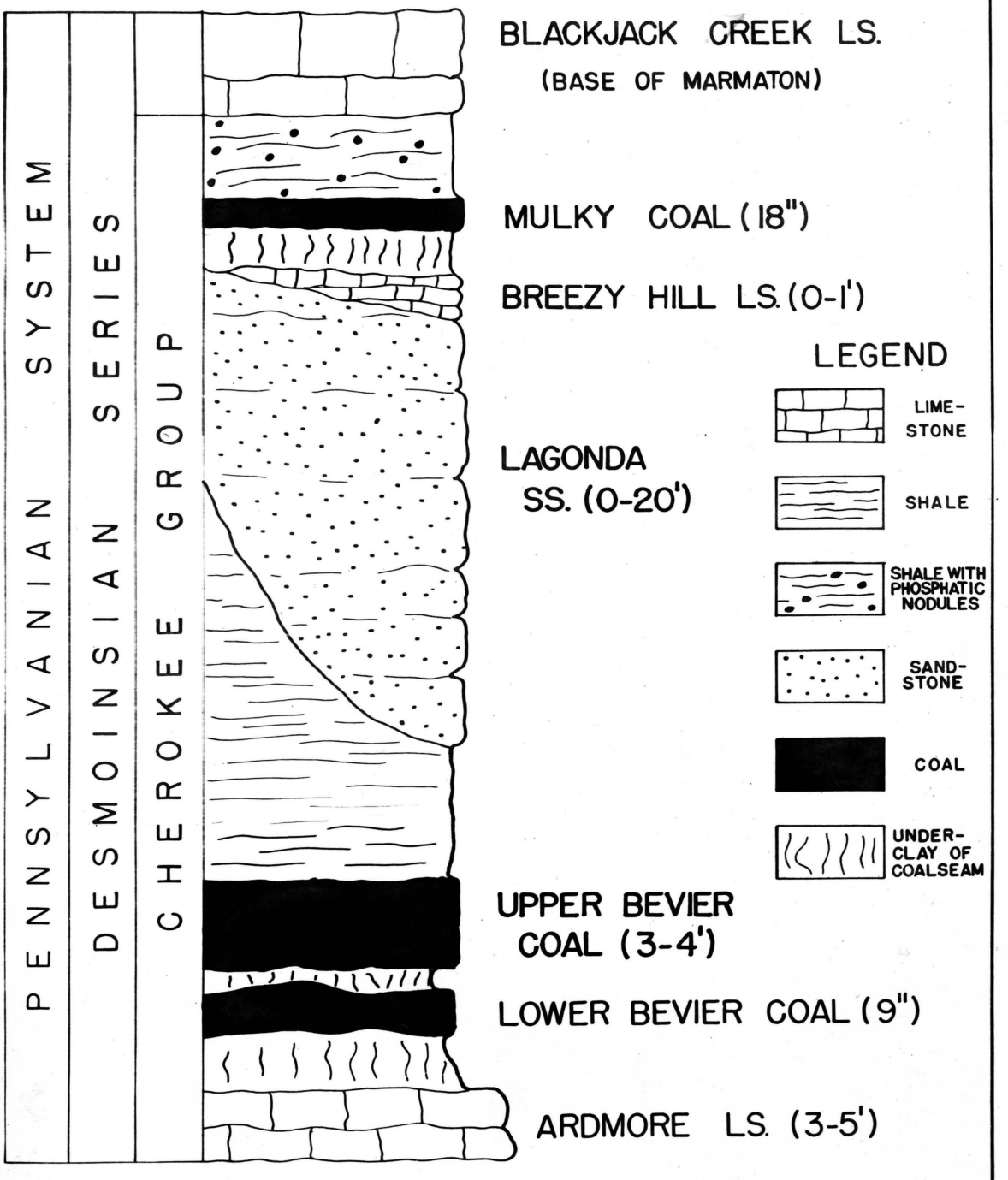


FIG. 2. DIAGRAMMATIC SECTION OF UPPERMOST CHEROKEE ROCKS IN MACON AND RANDOLPH COUNTIES.

The rock types present are shales, with some limestones, sandstones, and coal seams.

The Bevier seam is composite, consisting of two beds of coal separated by a thin shale band. The coal of both beds has approximately the same properties. The upper bed (locally called a "bench") of the Bevier coal consists of three to four feet of high volatile bituminous coal, with cleet fillings of pyrite, calcite and kaolinite. Figure 3 illustrates a section taken across a series of cleet fillings. The minerals present are calcite and pyrite. The block of coal was taken from locality 1, sample 3, (See Figure 7). The shale band is from zero to six inches thick, and is regarded as being the underclay of the upper bench of the Bevier seam. The lower bench of the Bevier seam consists of about nine inches of high volatile bituminous coal with cleet fillings of pyrite, calcite, and kaolinite. At certain horizons in the seam, pyrite is present as finely disseminated material through the coal. Figure 8 shows a pyrite rich horizon. No marcasite was found in the coal.

Beneath the lower bench of the Bevier coal lies one to four feet of gray underclay, sometimes containing stigmaria (fossil roots), but always containing some pyrite. McQueen (1943, p. 89) does not mention the underclay of the upper bench of the Bevier coal, but records that the underclay of the lower bench has no economic use in the ceramic industry.

The coal beds are nearly flat, the slight regional dip being towards the northwest. Occasionally the Bevier coal is

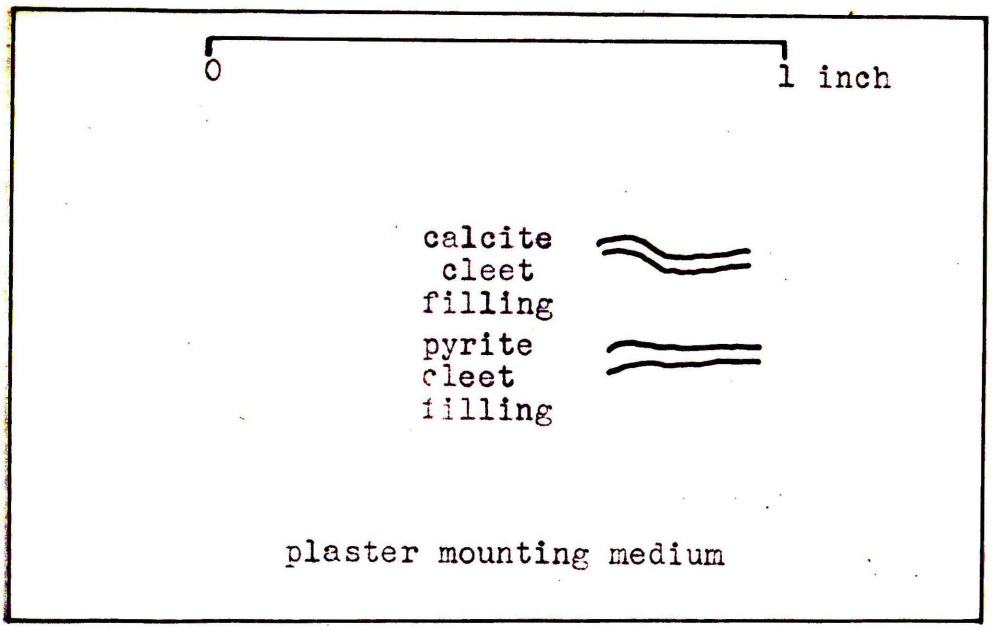


Figure 3. Pyrite and calcite cleet fillings from locality No. 1, sample No. 3.

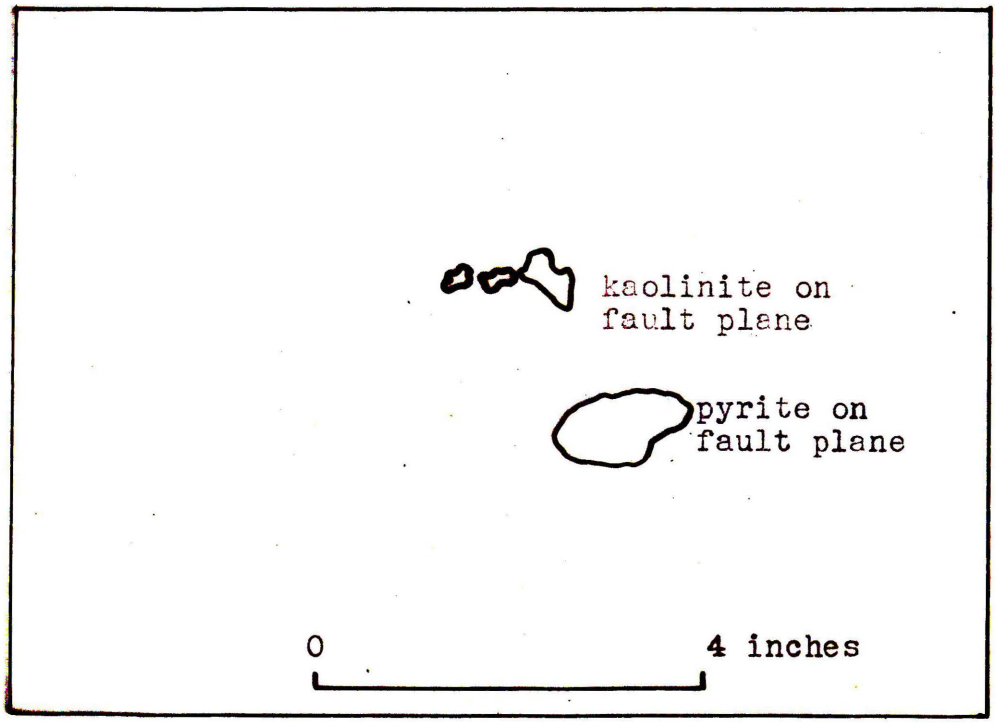


Figure 4. Coal block from fault plane, showing slickensides, with kaolinite and pyrite on the polished surface.

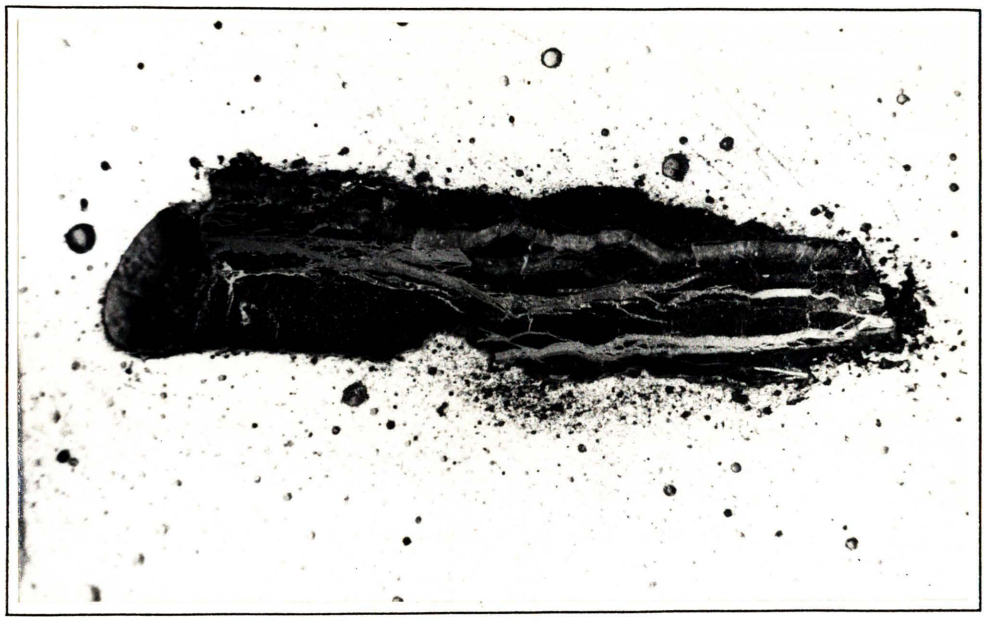


FIGURE 3

FIGURE 4

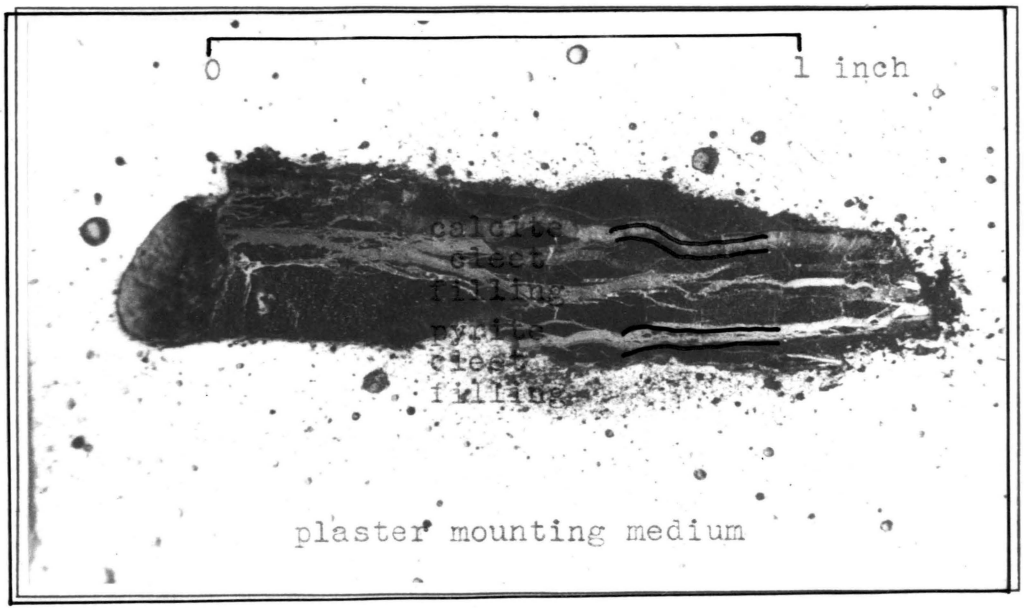


Figure 3. Pyrite and calcite cleat fillings from locality No. 1, sample No. 3.

FIGURE 3

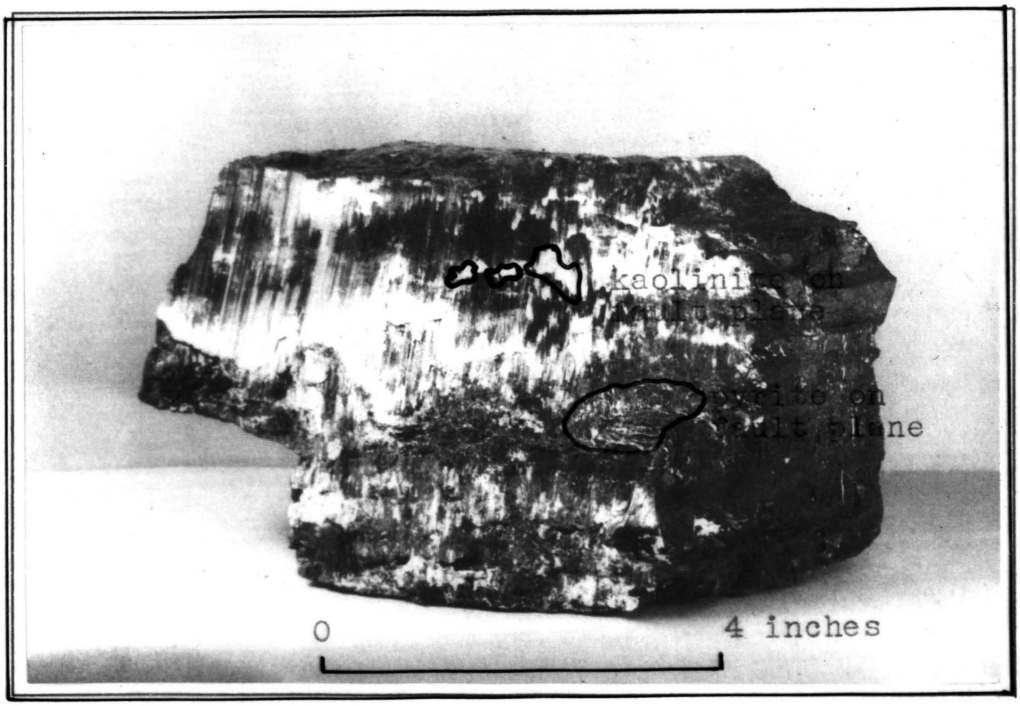


Figure 4. Coal block from fault plane, showing slickensides, with kaolinite and pyrite on the polished surface.

FIGURE 4

cut by small normal faults of very small throw. Figure 4 shows a block of Bevier coal from the footwall of such a fault, collected near locality 1. Total displacement was about one inch, yet the fault surface has been brought to a high degree of polish. X-ray diffraction investigation revealed that the white mineral on the polished surface was kaolinite. A small amount of crystalline pyrite was associated with the kaolinite.

In some parts of the area, glacial erosion (Pleistocene) has removed the overlying rocks, and glacial tills rest on the Bevier coal. In a few localities, the Bevier coal has also been removed, and the glacial tills rest directly on the Ardmore limestone.

HISTORICAL REVIEW

Exploration and production in the area.

The first record of the Bevier coal was by Hawn (1855, p. 126), who described a six-foot seam outcropping in Township 56 North, Range 15 West. Eighteen years later, Broadhead (1873, pp. 74-110) briefly described the geology of Macon and Randolph Counties, remarking that "the quality [of the coal] is generally good, but we find more or less Sulphuret of Iron [pyrite and/or marcasite] accompanying it." At that time there was very little organized mining of coal in the area, although farmers operated small mines for their own personal needs.

Winslow (1891, pp. 62-73) described the coal mines, and

by this time, coal was being produced in considerable quantities, from shaft mines and slopes, by both room and pillar and by longwall methods.

In 1893, Gordon (1893, pp. 1-75) mapped the Bevier quadrangle and published a geological report on the area.

Marbut (1898, pp. 311-371) mapped the Huntsville quadrangle, which joins the Bevier quadrangle on the south side.

Hinds (1912, pp. 270-308, 344-366) gave a detailed account of the geology of Macon and Randolph Counties, revising the Bevier and Huntsville quadrangles. At that time, intensive mining of the Bevier seam was in progress.

Statistics published by Searight (1949, pp. 41-52) show that Macon and Randolph Counties jointly have been responsible for approximately 25 per cent of the total production of coal in Missouri.

Development of coal petrology

The first thin sections of coal were produced by Witham (1832, p. 578). He recorded the presence of cellular bodies, and interpreted them to be vascular plants. Until the work of Von Guembal (1883, p. 1), two components were recognized in coal, "charcoal" (now called fusain) and "bituminous or compact" coal (the remainder). Von Guembal macerated coal to various degrees, using Schultze's solution, and watched the process of dissolution under the microscope. He came to the conclusion that an average coal is composed mainly of thin layers of alternating

"glanz" (now called translucent attritus), and "dull coal" (now called opaque attritus), with "charcoal" (fusain).

Modern concepts on coal petrology developed after the turn of the century. Theissen (1913) (American) and Stopes (1919) (English) proposed conflicting nomenclatures. Figure 5 gives a correlation between the two systems of nomenclature as recommended by the International Committee on coal petrology at Heerlen in 1935.

Sprunk and Theissen (1935, pp. 446-451) described experiments made in an attempt to correlate the proximate analysis, the ultimate analysis, and the coking properties with the petrographic properties of the coal. They found that bituminous coals of the correct rank, high in anthaxylon, are usually low in ash. Moreover they tend to produce good quality coke. Coals rich in spores have a high volatile content, but usually do not produce good coke.

Germanium in coal

Because of current interest in supplies of the rare element germanium, the Bevier coal samples were analysed for concentrations of this element.

Mendeleef, in 1867, forecasted the properties of a yet undiscovered element which he named eka-silicon. Nineteen years later Winkler (Sneed and Maynard, 1944, p. 744) first reported preparation of the so-called new element eka-silicon, which was renamed germanium. The source material which Winkler used was the rare mineral argyrodite (Ag_2GeS_6).

NOMENCLATURE OF COAL PETROLOGY

British and German terminology as recommended by the International Committee at Heerlen, 1935. Corresponding American terms are those used by the U. S. Bureau of Mines. This table is taken from Raistrick and Marshall, (1939, p. 271).

Macroscopic character of the coal.	British Nomenclature.		German Nomenclature.		American Nomenclature.	
	Rocktypes	Macerals (constituents)	Streifen-arten.	Gefuege-bestand-teile.	Coal types	Constituents.
Uniform brilliant black bands.	VITRAIN.	Vitrinite: translucent in thin section; cellular structure may or may not be well preserved: (a) Collinite-structureless; (b) Tellinite-structure preserved: (i) Xylinite-formed from wood tissues; (ii) Periblinite-formed from cortical tissues; (iii) Suberinite-formed from cork tissues.	VITRIT	Vitrinit	--	Anthraxylon. Term used to include the uniform brilliant bands (or their counterparts) in coals of all ages.
Charcoal-like layers and fragments which readily soil the fingers.	FUSAIN	Fusinite: cell structure well preserved. Cell walls opaque; cell cavities either empty, or occupied by mineral matter.	FUSIT	Fusinit		Fusain.
Bright coal; clearly laminated; composed of innumerable brilliant fragments and bands with some duller material.	CLARAIN	containing: Vitrinite; Resinite-resin bodies; } Translucent, orange-yellow in thin section. Exinite-which includes- (i) Cutinite-from cuticles (ii) Sporinite-from spores together with a little: Micrinite-granular opaque matter. Fusinite- as above.	CLARIT	 Micrinit Fusinit	Bright coal	Containing: Anthraxylon, Spores, Cuticles, Resins, etc. } Translucent Attritus. together with, Opaque and semi-translucent attritus. Fusain.
					SEMI-SPLINT COALS.	Intermediate in properties and constitution between bright and splint coal.
Dull coal: dull an nonreflecting in the hand specimen; lamination poor of absent.	DURAIN	Containing Fusinite, Micrinite, Resinite, Exinite, (i) Cutinite, (ii) Sporinite, and a very little Vitrinite.	DURIT		SPLINT COALS.	Very largely opaque and semitranslucent attritus with spores, cuticles, resin and a little anthraxylon.

Until the studies of Goldschmidt (1930, p. 398) were published, germanium was regarded as a very rare chemical curiosity. Goldschmidt showed that germanium tends to accumulate in coal seams and in naturally occuring iron-nickel alloys (meteorites).

Later, Goldschmidt and Peters (1933, p. 371) reported that some coal seams contain appreciable quantities of germanium, the richest reported being the Hartley Yard seam in Northumberland, Great Britain. The ash from this coal contained more than one per cent of germanium. Gibson and Selvig (1944, pp. 10-11) gave a review of the literature of the occurrence of germanium in coal ash, coal, flue dust, and coal-tar.

In the majority of coal ashes, the concentration of germanium is less than 0.05 per cent, and very few coal ashes contain more than 0.3 per cent. Ramage (1927, p. 783) showed that gallium, which also occurs as a trace element in coal, was considerably enriched in certain flue dusts, especially those dusts from producer gas plants. Morgan and Davies (1937, pp. 717-721) found that there was also an appreciable enrichment of germanium in flue dust, due to the volatility of germanous oxide. A manufacturer, desiring to produce germanium from coal, would probably not purchase a coal of high germanium content and burn it. More likely he would purchase flue dust from consumers of high germanium content coal.

In the United States the present production of ger-

manium is from zinc smelter residues. The only germanium producing plant operating in Great Britain at the present time is one producing germanic oxide from flue dusts. This British plant is handling, at an economic gain, flue dusts which contain more than 0.3 per cent germanium. The method of production follows very closely that described by Morgan and Davies (1937, pp. 717-721).

A report issued by Headlee and Hunter (1951, pp. 1-15) revealed that of the coal seams investigated, the high germanium concentrations were found within the top and/or bottom three inches of the coal seam. Shale partings also favored high concentrations. The germanium seemed to be concentrated in the organic matter of the coal by fluids circulating through the shales.

The importance of germanium today lies in the fact that small but essential quantities of the metal are used in the manufacture of transistors. Transistors are readily finding application in many electronic fields, replacing the more orthodox electronic tubes.

COLLECTING LOCALITIES

Three continuous sections ("column" or "pillar") were collected, two from a stripping pit of the Huntsville-Sinclair Coal Company, and the remaining one from a pit of the Bevier-Sinclair Coal Company. As near as possible to each continuous section a channel sample was taken. Figure 1 shows the collecting localities. The localities are as follows:

Section No. 1 From a pit of the Bevier-Sinclair Coal Company located SW¼, NW¼, sec. 6, T. 55 N., R. 14 W.

Section No. 2 From the south end of an active stripping pit of the Huntsville-Sinclair Coal Company, located in S½, SE¼, NW¼, sec. 33, T. 55 N., R. 15 W.

Section No. 3 Approximately 500 yards to the north of section no. 2, taken from the same pit. Location N½, SE¼, NW¼, sec. 33, T. 55 N., R. 15 W.

METHODS OF ANALYSIS

Sample Collection and Preparation

The methods of collecting and parparing the samples followed closely those outlined by Theissen, Sprunk, and O'Donnell (1938). A locality in the stripping pit was chosen where the coal was free from faults, slips and other disturbances. Due to the blasting of the overburden, the coal bed was always cracked to some extent, so a locality was chosen where these blasting fractures were at a minimum.

The section for examination was then obtained by breaking away the coal from either side of the "pillar." As the work proceeded, the pillar was found to split very easily along certain horizontal planes. These splitting planes are almost invariably fusain bands. As each of the blocks of coal were detached, the upper bedding plane was marked with a blob of yellow paint. This was to ensure that the block of coal would always be oriented the correct way. The blocks were carefully preserved in their correct order

for laboratory study. It was found that the pillar section could be obtained with the least difficulty if use were made of the natural fracture planes in the coal.

At the same locality, and as near to the pillar sample as possible, a channel sample was taken to obtain the average properties of the seam at that particular locality.

In the laboratory the blocks from one locality were laid out in their correct order, and sample positions marked out using a wax crayon. Cubes of coal approximately one inch in dimension were cut, (using a diamond saw) every three inches down the coal seam. A diamond saw was employed, because the coal smeared and clogged the cutting edge when a carborundum wheel was used.

The first sample taken was one in contact with the shale roof; the last in contact with the shale floor. If an especially interesting feature seemed to occur between two cube samples, a sample of the unusual material was collected. The cubes were reserved for thin section and/or polished surface studies.

From each thin section horizon another one inch cube was cut, and this was ground to pass through a 70 mesh Tyler screen and preserved in a stoppered bottle. This powdered coal was used for proximate analysis, and for tests for sulphur and crucible swelling number (free swelling index).

Each channel sample was crushed and quartered according to the British Standards method, and a representative sample obtained which would pass through a 70 mesh Tyler screen.

This sample was used for proximate analysis, and for estimations of the total sulphur, organic sulphur, and for the crucible swelling number.

The roof shale at locality no. 2 contained some thin stringers of coal approximately one-tenth inch inch thick. A sample of this roof shale was crushed to pass a 5 mesh Tyler screen, and then separated at specific gravities of 1.3 and 1.58, using float and sink methods. The liquids used were mixtures of acetone and acetylene tetrachloride. The three fractions, having specific gravities less than 1.3, 1.3 to 1.58, and greater than 1.58, were dried at 40° C. for several days. Intensive drying was necessary to remove all traces of the separation liquids, so as to prevent the formation of volatile germanic chloride on ashing the coal sample. Headlee and Hunter (1951, p. 12) lost one third of the germanium content of gravity separated coals when ashing. This loss was attributed to the fact that carbon tetrachloride remained in the coal and combined with the germanium to give volatile germanic chloride ($GeCl_4$) which was lost in the ashing process.

Polished Section Technique

The polished section technique adopted was very similar to that described by Raistrišk and Marshall (1939, p. 264). The block to be studied was first smoothed on a coarse carborundum block lubricated and cleaned with a stream of running water. This initial smoothing was to remove any surface irregularities left by the diamond saw. The

block of coal was washed to remove any loose particles of coal, and ground very gently, first on a coarse grained Belgian hone and then on a fine grained Belgian hone. The hones were kept cleaned by running water. After the fine honing, the surface was given a final polish using Selvyt cloth and Goddards Silver Plate Polish. Prolonged polishing with the silver plate powder will produce a marked relief effect, and this may be very desirable for showing up the coal structure. This relief polishing, however, should be avoided in thin section preparation. Figure 9 shows a portion of a thin section containing disseminated pyrite. Each dark area contains a small grain of pyrite which, because of its hardness, has prevented the grinding of the slide in that area to its correct thickness.

The polished sections were examined microscopically using vertical illumination in the same manner that polished metals and ore minerals are studied.

Thin Section Technique

The procedure for the preparation of a thin section of coal is identical with that described under "polished section technique" until a polished face has been produced. After a plane face had been polished on the block of coal, all water was removed by prolonged drying of the coal at 105° C. If the water is not removed, it vaporizes and causes bubbles in the cement layer between the coal and the glass. After the polished block had been dried, it

was placed, polished face down, on a clean piece of paper on an electric hot plate at 140° F. (60° C.). A piece of Lakeside no. 70 thermosetting plastic was placed on a microscope slide which previously had been frosted and then had been washed in carbon tetrachloride to remove all grease contamination of the surface. The slide with the cementing medium was heated on the hot plate with the coal. After both had heated up to 140° F. (60° C.). the block was lowered edge first into the cement pool on the slide. By doing this, the danger of entrapping air in the cement was reduced to a minimum. The slide and coal were then allowed to cool under steady pressure. Bubbles which may develop tend to be forced out at the sides of the block. Care was taken, so that when the pressure was applied, the center of the slide was supported, otherwise the slide would bend slightly producing a cement layer thicker in the middle than at the edges. Such a cement layer would cause the center of the thin section to be ground away, before the edges reached proper thickness.

The cement-to-glass union was stronger if the surface of the glass slide was frosted before mounting the coal block. The frosting was done by grinding one face of the glass slide with 600 carborundum on a glass plate.

After the cement had solidified, the slide was carefully examined for trapped bubbles. If any bubbles were seen, then the coal block was remounted.

Workers of the U. S. Bureau of Mines used a mixture of Canada Balsam and marine glue as the cementing medium.

Workers of the Illinois Geological Survey use Lakeside no. 70 thermosetting plastic. The Canada balsam-marine glue mixture must be prepared by heating in a pot, whereas the Lakeside no. 70 can be purchased ready for use. In this problem Lakeside no. 70 thermosetting plastic was used because of convenience.

After cementing, the excess coal was cut away using a diamond saw, leaving about one-eighth inch thick layer of coal on the slide. This thick slice of coal was reduced in thickness to about one thirty-second inch using a rotating lap wheel and 180 carborundum powder. After washing thoroughly to remove all abrasive, the thin slice was ground on a carborundum block, to remove as much coal as safety would permit, and to even out the thickness if the lap wheel had produced a wedge shaped section.

When the coal slice was about paper thickness, grinding was begun on the coarse Belgian hone. At this stage, the coal was still opaque, except for small cracks and fissures which transmit the light. The hone was kept well lubricated with running water, and grinding carried on until the edges of the thin slice began to appear red, in transmitted light. Grinding was continued on the fine hone. In the last stages of the grinding, the edges of the thin section were usually lost, because the edges reached the required thickness before the middle.

Finally, the ground surface was polished using Goddards plate powder, applied with a soft cork. The polished surface was washed to remove any abrasive, allowed to dry,

and protected with a cover slip using diaphane cement.

In the literature, the use of Goddards plate powder, is recommended. Goddards plate powder is difficult to obtain, as it is produced in England. There are many polishing powders available in the United States, and investigation should be made to locate a substitute.

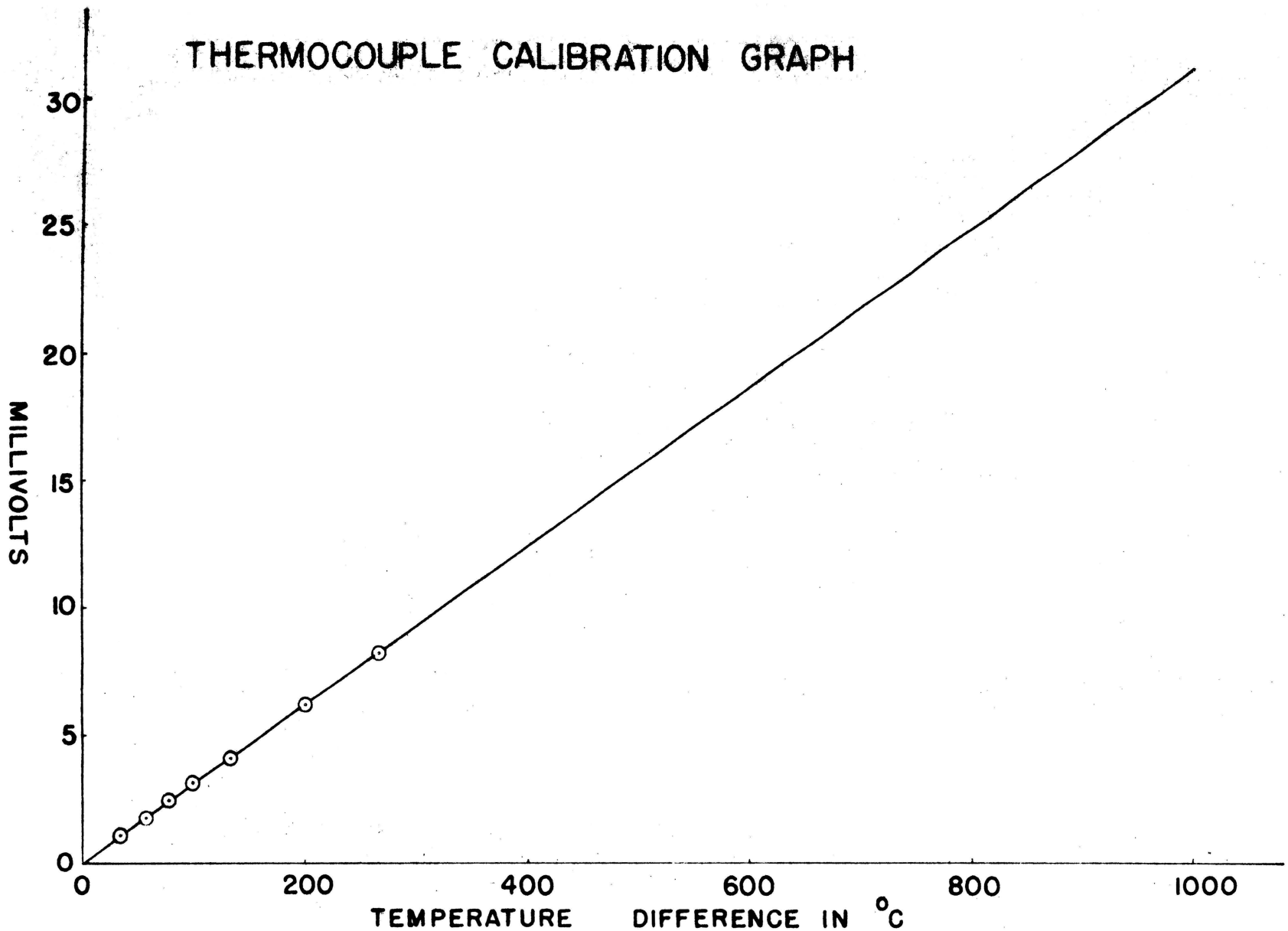
A thin section produced by this method may vary from three to seven microns in thickness. This compares with 30 microns, which is the standard thickness of a petrological section of an igneous, metamorphic or sedimentary rock.

Thermocouple Calibration

Accurate knowledge of the temperature is necessary in performing tests for sulphur content, volatile content, and crucible swelling number. As a tool for determining temperatures in these tests, a chromel-alumel thermocouple was manufactured in the Ceramic Department of the Missouri School of Mines. The fixed points used in the calibration were the melting point of tin (232° C.), and the boiling point of water (100° C. at 760 mm. mercury pressure). Figure 6 shows the calibration curve. The voltage produced by the thermocouple was found to vary linearly with the temperature difference between the hot and cold junctions.

Ash Determination

Determination of percentage of ash or incombustible matter is important in evaluating coal. For this purpose


THERMOCOUPLE CALIBRATION GRAPH
MILLIVOLTS
0
5
10
15
20
25
30
0
200
400
600
800
1000
TEMPERATURE DIFFERENCE IN °C

one gram of powdered coal was heated in a large low-type porcelain crucible at a temperature of 775° C. After all the carbonaceous matter had been oxidized (about one hour), the crucible and contents were cooled in a dessicator and weighed. The ash content of the coal was computed on a percentage basis of the total coal taken. The ash samples were preserved in small vials to be used for germanium studies.

Sulphur Determinations

Total quantity of sulphur. The total quantity of sulphur in each sample was determined by the method of Eschka (British Standards Institution, 1942, p. 43). One gram of the powdered coal sample was well mixed with approximately three grams of Eschka mixture. The eschka mixture was prepared by mixing two parts by weight of calcined magnesium oxide with one part by weight of anhydrous sodium carbonate. A blank test is necessary, as the Eschka mixture contains some sulphur. The coal and Eschka mixture were transferred to a large porcelain crucible, and covered with one gram of pure Eschka mixture. The crucible was heated gently to ensure slow expulsion of the volatile matter, and after about ten minutes the temperature was raised in small stages until it reached 800° C.±25° C. after one hour. This temperature was maintained for one and a half hours. During the last half hour, the mixture was stirred with a platinum wire to promote oxidation.

The contents of the crucible were transferred to a beaker by washing with 100 ml. of warm distilled water

The suspension in the beaker contained all the original sulphur of the coal in the form of sulphides of magnesium and sodium. The suspension was digested with 10 ml. of saturated bromine water to oxidize the sulphides to sulphates. Concentrated hydrochloric acid was added to make the suspension acid, and the excess bromine was boiled off. The ash was filtered off and washed, and the washings added to the filtrate.

The filtrate was cooled, and neutralized with ammonium hydroxide solution, and then one ml. of concentrated hydrochloric acid added to put the pH just on the acid side of neutrality. Whilst the solution was boiling, 10 ml. of barium chloride solution were added slowly with constant stirring. The solution with its precipitate of barium sulphate was allowed to stand in a warm room overnight to ensure that precipitation was complete. The precipitate of barium sulphate was filtered and washed until the washings gave only a faint trace of opalescense with silver nitrate solution. The filter paper was dried and ignited, and the residue moistened with nitric and sulphuric acids to oxidize the ash. The weight of the sulphur in the original coal sample was calculated from the weight of barium sulphate using the conversion factor 0.1373.

"Sulphate" sulphur

The "sulphate" sulphur was determined as described by British Standards Institution (1942, p. 45), the method

being based on a technique developed by Powell (1921, p. 1). As the amount of "sulphate" sulphur is usually small, five grams of the powdered coal were taken. The coal was placed in a beaker and covered with 300 ml. of dilute hydrochloric acid (one part acid to 60 parts water). The beaker was covered and allowed to stand at a temperature of 60° C. for fourty hours. The mixture was filtered through a quantitative filter paper and the residue washed with warm dilute hydrochloric acid (same strength as before). The washings were added to the filtrate, and the residue was discarded. Two ml. of bromine water were added to the filtrate, to ensure that all the sulphur was present in the sulphate state. The excess bromine was boiled off. The solution was adjusted for acidity as before, and the sulphate precipitated as barium sulphate. The weight of barium sulphate X 0.1373 gave the weight of sulphur present in the sulphate stage of oxidation in five grams of coal.

"Pyritic" sulphur. The "pyritic" sulphur was found by allowing one gram of the powdered coal to stand with 80 ml. of dilute nitric acid (one part acid to four parts water), for twenty four hours with occasional stirring. A few drops of bromine water were added to aid the oxidation. At the end of the extraction period, the acid solution was separated from the unreacted coal by filtration. The residue was washed with dilute nitric acid (same strength as that used previously) and the washings added to the filtrate.

The filtrate was evaporated to dryness in a large

beaker, and the residue dissolved in 30 ml. of dilute hydrochloric acid (one part acid to six parts water). The acidity was adjusted as before, and the sulphate precipitated as barium sulphate. This analysis determined the total amount of sulphur in inorganic combination. The weight of barium sulphate X 0.1373 gave the weight of sulphur in the coal.

The weight of "sulphate " sulphur is already known from the previous determination, so the weight of "pyritic" sulphur can be calculated by subtraction.

"Organic" sulphur. The "organic" sulphur was found by difference. The total sulphur content of the coal (as found by the Eschka method) minus the total sulphur found in the "pyritic" analysis, gave the concentration of "organic" sulphur in the coal.

Determination of Volatiles

Dry basis. The method outlined in British Standards Institution (1942, p. 25) was used. One gram of coal was heated for seven minutes at a temperature of 925° ± 15° C. in a fused silica crucible with lid. The loss in weight of the coal is defined as the volatile content, after an adjustment has been made for the moisture content of the coal. The moisture content of the coal was found by drying one gram of powdered coal in an oven at 105° C. as described in British Standards Institution (1942, p. 13). The moisture content of the coal is defined as the loss in weight when the coal is heated under the conditions just mentioned.

Dry, ash free basis. This was computed using the data found in the volatile, dry basis determination. An allowance

was made for the ash content of the coal, as well as for the moisture content.

Determination of crucible swelling number

(Free swelling index)

One gram of powdered coal was heated for two and a half minutes in a silica crucible with lid. The crucible and burner were protected by a draft shield, six inches long, and four inches internal diameter. The draft shield was made by lining a fruit juice can with thick asbestos paper. The dimensions of the crucible and of the draft shield were as defined in British Standards Institution (1942, p. 64). The temperature of coking was 825° ± 5° C. The temperature was checked by placing the thermocouple inside a crucible, which had been heated for 15 minutes.

After heating, the coke button was allowed to cool, and its outline compared with the standard outlines (British Standards Institution, 1942, p. 69). The swelling number of the button was that number inscribed in a standard outline, to which the maximum dimensions of the coke button most nearly matched. Four buttons were made for each coal sample, and the swelling index recorded as the average of the four values obtained.

Germanium determination

After an ash determination had been made, the ash was preserved for germanium estimation by a spectrographic

method. Spectrographic determinations for germanium were performed under the supervision of Dr. E. E. Pickett at the University of Missouri.

The coal ash of each of the channel samples were prepared in an endevour to keep the germanium loss at a minimum. An ashing method recommended by Morgan and Davies (1937, p. 717) was used. The coal was ashed in a thin layer, and the contents of the crucible repeatedly moistened with concentrated nitric acid. This treatment prevented the reduction of the germanium from the quadrivalent state to the bivalent state, by preserving oxidizing conditions in the coal while ashing was in progress.

Six samples of ash from locality no. 2 were analyzed, in order to make more probable that the highest and lowest concentrations of germanium would be ascertained (Headlee and Hunter, 1951, p. 14). Table 5 lists the germanium concentrations in parts per million of ash, in the samples which were analyzed.

Determination of calorific values

Calorific value determinations were performed on the channel samples from the three localities. The calorific values were obtained for comparison with published analyses.

The coal sample was burnt in a steel bomb containing oxygen at 20 atmospheres pressure, which was immersed in a water filled calorimeter. The temperature rise was noted, and the heat liberated in the combustion of the coal was computed.

Corrections were made for the heat lost by radiation, for the heat generated by the combustion of the iron wire used to ignite the coal, and for the acids produced by the combustion of the sulphur and nitrogen in the coal.

Refractive index of anthraxylon

Samples of bright coal from localities no. 1, 2, and 3 were crushed to a fine powder, and the refractive index of the translucent particles found using the oil immersion method. A small amount of the coal powder was placed on a microscope slide and a cover slip placed on top. A drop of oil of known index of refraction was placed at the edge of the cover slip. Capillary attraction drew the oil under the cover slip. The refractive indeces of the oil and of the translucent particles were compared, using the Becke line. Different oils were used, until a match in refractive index was obtained.

RESULTS OBTAINED

Searight (1949, p. 17) described the Missouri coals of Pennsylvanian age as "high volatile bituminous." The American Society for Testing Materials (A. S. T. M.) defines a high volatile bituminous coal as having fixed carbon content of less than 69 per cent, and a calorific value greater than 11,000 B. T. U. per pound.

Table 1 shows four analyses of the Bevier seam, from published sources, compared with the analyses of the three channel samples. The coal from the localities studied has approximately the same properties as the coal previously

Table 1.

Analysis data for the Bevier coal (both benches) from published sources, with analysis data from localities no. 1, 2, and 3.

All analyses on a moisture free basis.

Locality	Ash %	Volatile matter %	Fixed carbon%	Sulphur % total	pyritic	sulphate	organic	B.T.U.	B.T.U. ashfree	Source of information
Mark Twain Mine Huntsville.	9.72	44.00	46.28	4.20				12571	13924	56 Ann Rept. Mo. Dept Mines 1943.
Macon County	11.10	39.40	49.50	3.80				12988	14610	63rd Ann Rept. Mo.Dept.Mines 1950
1¼ miles SE Bevier.	11.22	39.86	48.92	4.07				12686	14351	Hinds, (1912, p.432)
Huntsville (S. End)	11.81	40.33	47.86	5.98				12656	14351	Hinds, (1912, p.434)
Locality No. 1 (Macon Co)	14.33	37.04	49.73	3.07	1.28	0.49	1.30	12476	14563	
Locality No.2 (Randolph Co)	12.67	38.17	49.26	5.05	3.20	0.21	1.64	12705	14548	
Locality No. 3 (Randolph Co)	18.29	34.29	47.42	6.14	4.84	0.15	1.15	11048	13520	

described.

Microscopic studies of the translucent fragments of powdered coal from the channel samples, showed that the refractive index ranges from 1.75 to 1.76. This range is similar to that of high volatile bituminous coals from Illinois which were investigated by McCabe (1937, p. 447).

The calorific values of the coal at the three localities range from 13,520 to 14, 563 B. T. U. per pound (mineral-matter-free basis). These values of calorific value place the coal studied in the "high volatile bituminous (A)" group of the A. S. T. M. classification.

The ash contents at the channel sample localities are higher than those in published data on the Bevier seam. Hinds (1912, p. 421) reports that "in cutting the sample [for analysis] care was taken to exclude such impurities - bony layers, shale partings, sulphur lenses, streaks - as are commonly rejected in mining and preparing the coal at the mine." The high ash content of the channel samples might be attributed to insufficient hand picking of the impurities before the coal was prepared for analysis.

Concentrations of germanium in the ash samples ranged from 50 to 100 parts per million of ash, (0.005 to 0.01 per cent) (see table 5). Low concentrations such as these cannot be extracted at economic gain under present day conditions. However, boilers and furnaces consuming the Bevier coal from this locality may concentrate the small amount of germanium in the flue dust. In the spectrographic determination of

germanium, the following elements were also found in very small concentrations: cobalt, zinc, nickel, copper, lead, tin, boron, molybdenum, vanadium, silver, cadmium, and gallium.

The channel samples contained quantities of sulphur. "Pyritic" sulphur accounted for about one half of the total sulphur present. "Organic" sulphur ranked second in quantity present. "Sulphate" sulphur was present only in small amounts. Examination of the samples collected revealed that the pyrite was present in two distinct forms, as cleet fillings (Fig. 3), and as disseminated material (Fig. 8). The surface of the pyrite in the cleet tarnished to a bronze luster. The disseminated pyrite was unstable, and decomposed into basic iron sulphates if placed in a moist atmosphere for a few hours. The reason for this difference in stability is not known with certainty, but it may be due to difference in particle size.

The instability was not due to marcasite being present, as X-ray diffraction photographs were made, and these contained only lines attributable to the pyrite crystal structure. No lines were found in the diffraction patterns which would correspond to marcasite. In a section through a disseminated pyrite band, taken perpendicular to the bedding planes, the small pyrite grains have an outline approximately oval in shape. The major axis of the oval is parallel to the bedding planes of the coal (see figure 8). It may be that maximum growth took place along the bedding planes, because of favorable permeability characteristics in the plane of the bedding.

Apart from the shale bench, which separates the two coal benches, there appear to be no obvious features of stratigraphic correlation between the three localities, which could be ascertained by this study. The minimum value of the total sulphur content in any of the samples analysed was just over two per cent, this figure being constant over considerable thickness of the seam in localities No. 2 and 3.

Detailed section studies

Tables 2, 3, and 4 contain analysis data for the detailed samples from localities No. 1, 2, and 3. Figure 7 shows these results plotted graphically. The relative proportions of anthraxylon and attritus, as determined in thin section, have no obvious relationship with any of the properties determined. This lack of correlation should not be regarded as important, however, because of two sources of error, both of which give erroneous values for the proportions of petrographic ingredients. The relative proportions were estimated by eye. In thin section preparation, the edges of the section were invariably lost before the section was completed, and because of the banded character of the coal, the material finally studied under the microscope was not necessarily representative of the sample which was analysed chemically.

The ash contents of the samples, at a given locality, vary with position in the seam. High ash percentages are caused either by disseminated pyrite bands or by thin shale stringers. Because of the low concentration of "sulphate" sulphur, this was believed to be of minor importance in the

FIGURE 7.

GRAPHS SHOWING RELATIONSHIPS BETWEEN PETROGRAPHIC PROPERTIES, ASH CONTENT, SULPHUR CONTENT, CRUCIBLE SWELLING NUMBER, AND VOLATILE CONTENT OF COALS FROM LOCALITIES No. 1, 2, & 3.

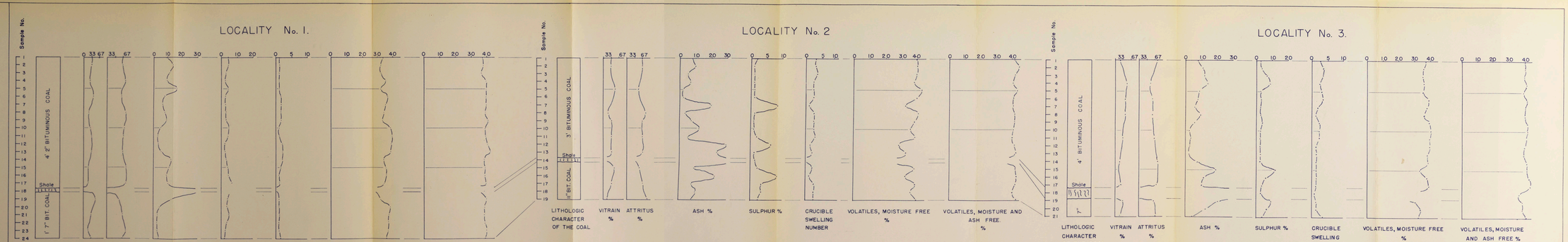


Table 2

Analysis data for samples from locality No. 1.

Sample No.	Ash %	Sulphur %	Crucible Swell, No.	Volatiles Dry basis	Volatiles Ash free
1.	9.73	4.33	1	33.42	36.92
2.	13.59	4.20	1	32.56	37.71
3.	11.35	2.87	1	32.54	36.73
4.	9.58	2.40	1	35.85	39.67
5.	16.45	4.31	1	32.75	39.25
6.	7.69	2.38	1½	36.69	39.76
7.	6.35	2.67	1½	35.86	39.42
8.	7.04	2.84	1½	34.61	38.97
9.	9.17	2.91	1½	33.82	40.49
10.	5.32	4.94	1	38.42	38.95
11.	3.30	4.08	1	39.81	39.96
12.	3.51	2.36	2	39.26	40.62
13.	5.49	2.41	2	38.76	42.45
14.	12.38	2.41	2	34.31	38.37
15.	10.79	4.27	1½	36.02	39.19
16.	9.34	4.83	1	36.14	38.75
17.	10.41	6.79	1	34.92	39.83
18.	73.42	-	-	-	-
19.	12.83	4.32	1	32.47	39.87
20.	4.26	3.78	1	38.51	38.64
21.	2.94	4.84	1	37.92	38.49
22.	2.56	3.51	1	37.48	39.06
23.	3.04	2.76	1	37.42	39.63
24.	3.77	2.28	1½	36.26	39.22

Table 3

Analysis data for samples from locality No. 2.

Sample No.	Ash %	Sulphur %	Crucible Swell, No.	Volatiles Dry basis	Volatiles Ash free
1.	7.53	3.38	3	39.35	41.74
2.	9.81	2.16	3	39.94	44.28
3.	5.21	2.20	3½	39.71	41.92
4.	6.68	2.37	2½	37.74	40.45
5.	1.72	2.34	2½	42.72	43.48
6.	2.10	2.36	2½	39.85	40.70
7.	19.81	16.80	1	32.46	40.52
8.	3.01	2.16	2½	40.60	41.85
9.	7.70	2.14	2½	38.18	41.37
10.	12.62	2.14	2½	35.51	40.62
11.	5.06	3.93	3	38.39	40.44
12.	31.21	12.94	1½	28.27	42.12
13.	23.65	2.60	2	32.80	42.97
14.	89.27	2.97	1	8.37	81.89
15.	9.63	4.51	2	37.97	42.02
16.	22.49	16.54	1	32.62	42.20
17.	7.67	6.37	2½	37.98	41.17
18.	10.15	6.63	2½	36.01	40.08
19.	8.18	5.68	2½	39.03	42.46

Table 4

Analysis data for samples from locality No. 3.

Sample No.	Ash %	Sulphur %	Crucible Swell, No.	Volatiles Dry basis	Volatiles Ash free
1.	7.23	2.72	4	37.09	39.93
2.	11.16	3.26	3½	35.96	40.48
3.	12.10	6.51	3½	35.47	40.37
4.	13.79	8.45	2½	35.78	41.74
5.	8.69	2.42	3	35.66	39.06
6.	7.19	2.98	3½	38.90	41.91
7.	6.04	2.40	2	38.24	40.71
8.	9.60	2.40	1½	36.56	40.49
9.	5.82	3.29	2½	39.41	41.85
10.	2.47	2.49	2½	41.08	42.12
11.	3.31	2.36	2½	40.23	41.61
12.	2.91	2.43	1½	39.89	40.40
13.	2.31	2.32	1½	38.61	39.53
14.	7.27	2.38	1½	38.75	41.78
15.	19.35	11.32	1½	33.65	41.73
16.	11.78	5.80	1½	37.81	42.84
17.	10.27	3.66	1½	39.24	43.71
18.	43.83	2.90	1	21.30	37.80
19.	20.74	9.28	1½	31.13	39.15
20.	12.97	6.50	1½	34.00	38.95
21.	4.17	3.83	3½	37.98	40.94

Table 5

Data for the coal ash samples analyzed for germanium.

Locality and sample no.	Position of sample in seam.	Concentration of germanium in ash in parts per million.
Locality No. 1.	Channel sample.	50
Locality No. 2.	Channel sample.	100
Locality No. 3.	Channel sample.	100
Locality No. 2, sample No. 01A.	Coal stringers in roof shale. Sp. Gr. less than 1.3	100
Locality No. 2, sample No. 01C.	Shale roof. Sp. Gr. greater than 1.6	5
Locality No. 2, sample No. 6.	15 inches down from roof of seam.	100
Locality No. 2, sample No. 13.	Just above shale bench.	5
Locality No. 2, sample No. 19.	In contact with floor of seam.	100
Locality No. 2 sample No. 10	27 inches down from roof of seam.	5

Table 6

Proportions of Anthraxylon and Attritus seen in thin section.

Locality No. 1.			Locality No. 2.			Locality No. 3.		
sample no.	anthraxylon %	attritus %	sample no.	anthraxylon %	attritus %	sample no.	anthraxylon %	attritus %
2	30	70	2	30	70	1	20	80
4	20	80	5	50	50	4	50	50
6	40	60	8	20	80	6	40	60
8	20	80	9	30	70	8	40	60
10	25	75	11	30	70	11	30	70
11	30	70	13	30	70	14	20	80
13	30	70	15	40	60	17	25	75
15	20	80	17	30	70	19	30	70
17	20	80	19	10	90	21	20	80
19	50	50						
21	30	70						
23	20	80						

sulphur analysis figures. On either border of the shale bench, which divides the Bevier seam into two parts, the ash contents of the samples are high. This means that there is a gradational change from bituminous coal to shale, and back to bituminous coal.

The graphs of sulphur content of the coals show that the concentration of sulphur did not fall below about two per cent. This figure is regarded as a "background" concentration of sulphur, and is believed to be made up of the organic sulphur content, plus sulphur present as finely disseminated pyrite (Fig. 9). Bands rich in disseminated pyrite increase the sulphur concentration to much higher than the "background" value.

Crucible swelling number determinations show that the coal is not homogeneous with regard to swelling properties. Swelling numbers ranged from 1 to 4½, and some samples were non-agglomerating. The swelling number was affected unfavorably by large quantities of sulphur or mineral matter in the coal.

Volatile percentages (on a dry basis) range from 28 to 43 per cent, and the volatile curve shows negative correlation with the ash content of the coal.

Volatile contents (on ash free basis) range from 37 to 43 per cent, a much smaller range than those for the values from the volatile determinations on the dry basis. The volatile values from the samples of locality no. 1 are consistantly less than those of localities no. 2 and 3. The lower volatility of the coal at locality no. 1 is not apparent in

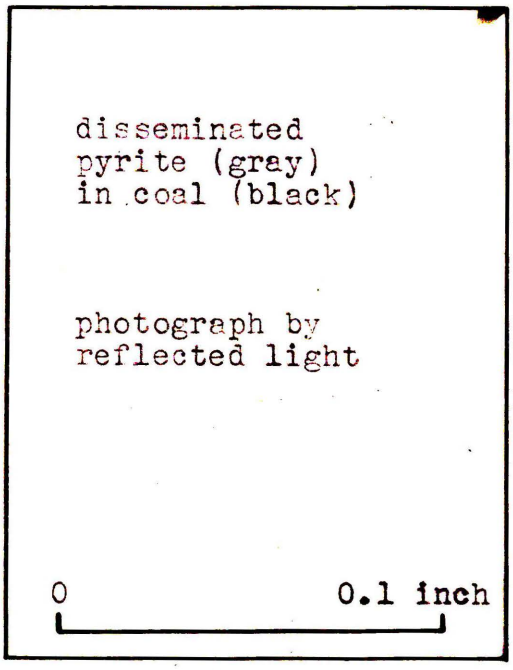


Figure 8. Disseminated pyrite in coal.

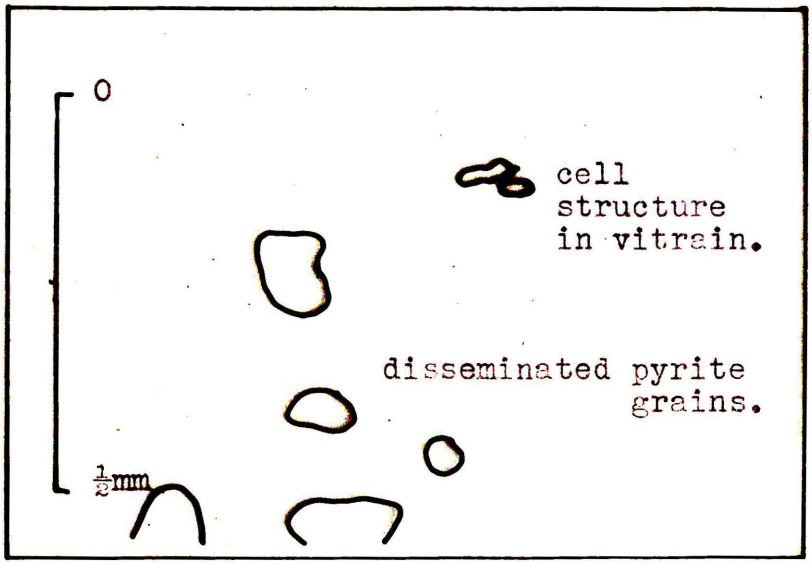


Figure 9. Disseminated pyrite in vitrain.

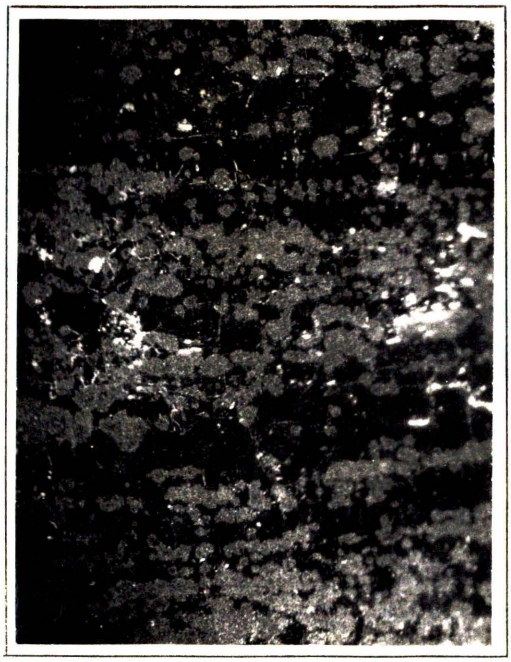


FIGURE 8

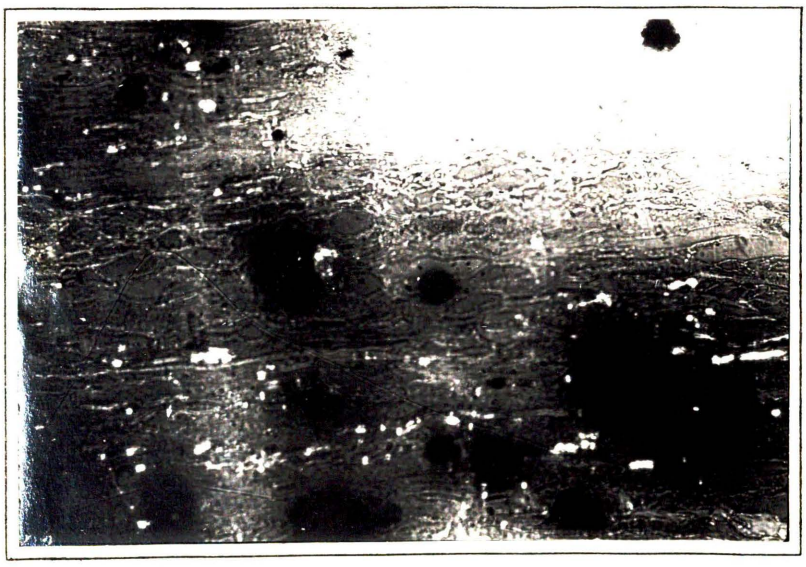


FIGURE 9

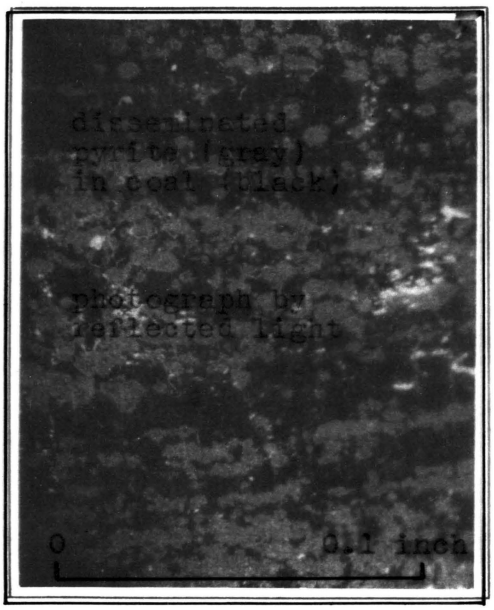


Figure 8. Disseminated pyrite in coal.

FIGURE 8

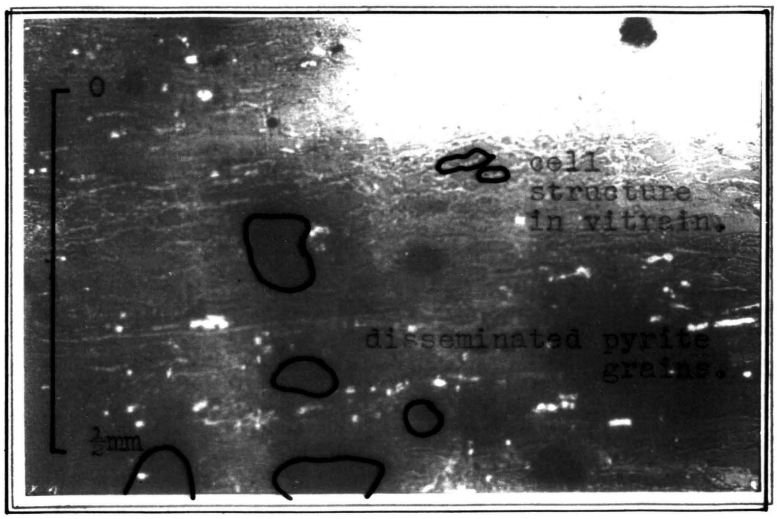


Figure 9. Disseminated pyrite in vitrain.

FIGURE 9

the analysis data for the channel sample at that locality, but the detailed analyses do indicate a slightly higher rank for the coal at locality no. 1. The discrepancy in the rank, as indicated by the channel sample and by the detailed sample, may be due to bands of high volatile coal which lay between the detailed samples. The discrepancy may be due to the fact that the channel sample was not a representative sample for locality no. 1.

Locality No. 1

Table 2 gives the detailed analyses figures for the samples from locality no. 1. Some peaks in the ash curve correlate with peaks in the sulphur curve. These peaks are due to pyrite in the coal. Other sulphur peaks have no corresponding ash peaks, indicating that "organic" sulphur was responsible. ~~No consistant values of "background" sulphur was responsible~~. No consistant values of "background" sulphur are present.

The coal at locality no. 1 was very poor swelling properties. The top 18 inches of the seam were non-agglomerating. Lower down in the seam, the coal did agglomerate, but nowhere produced a coke with cellular texture. The volatile content of the samples ranged from 37 to 43 per cent on the ash free basis.

Figure 10 shows a photomicrograph of part of a thin section of sample no. 8. All photographs were taken slightly out of focus, so ~~far~~ as to make the Becke line effect emphasize the cell structure in the anthaxylon. The material in Figure 10 is mainly anthraxylon with some resin bodies.

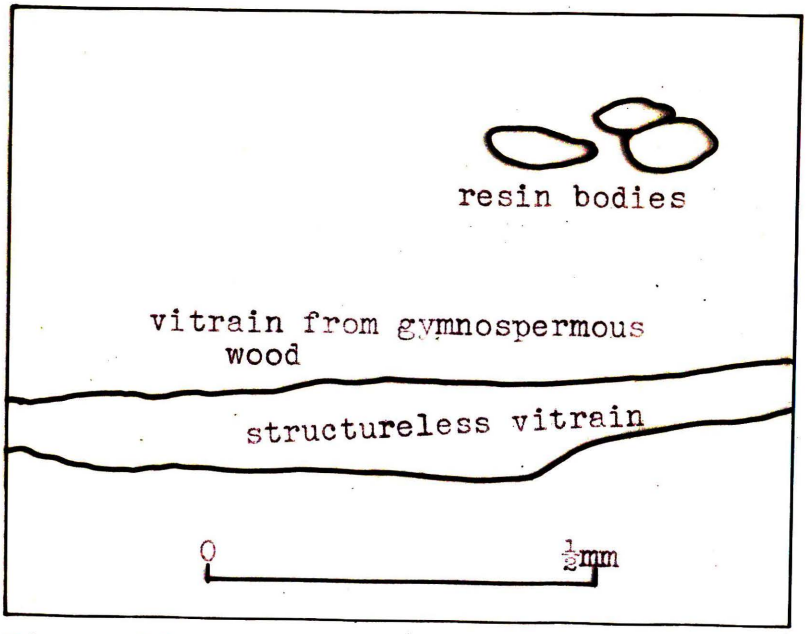


Figure 10. Gymnospermous vitrain with resins.

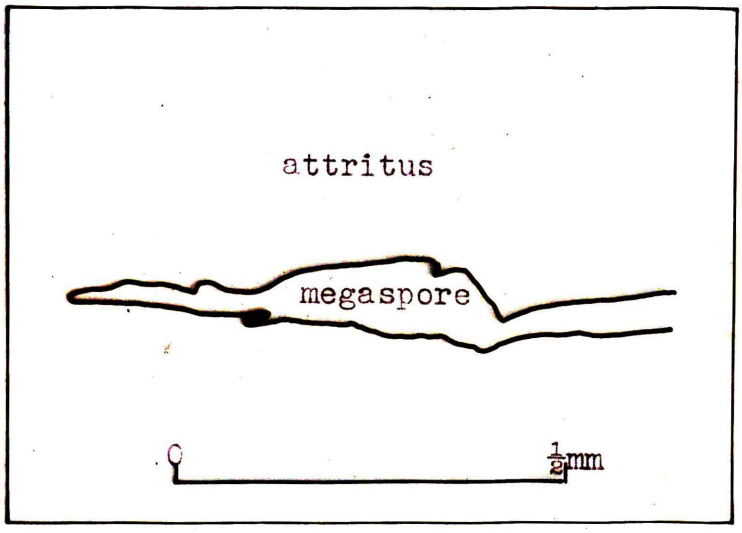


Figure 11. Megaspore(s) in attritus.

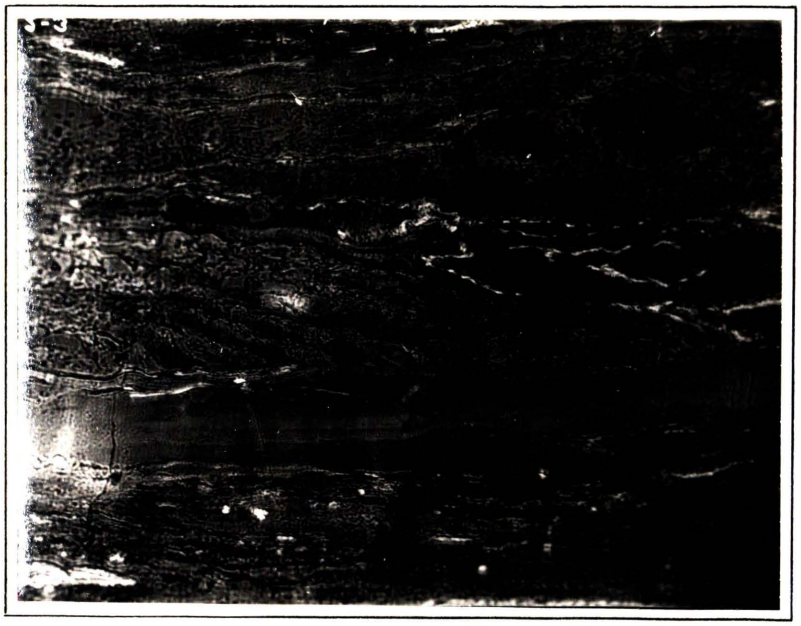


FIGURE 10

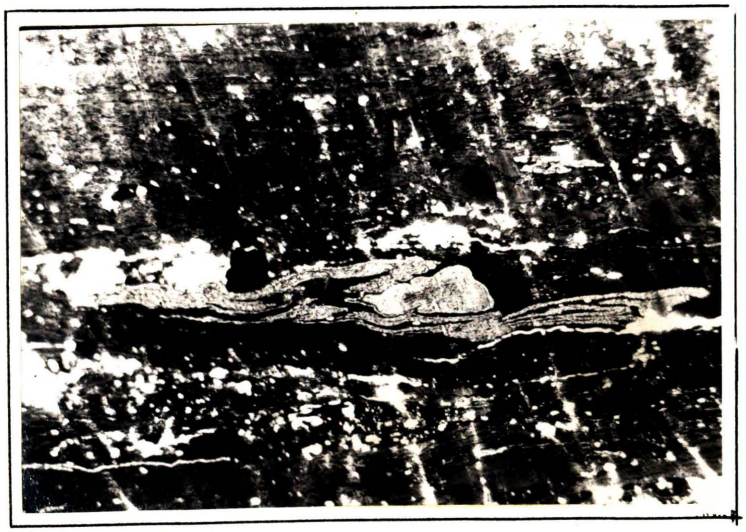


FIGURE 11

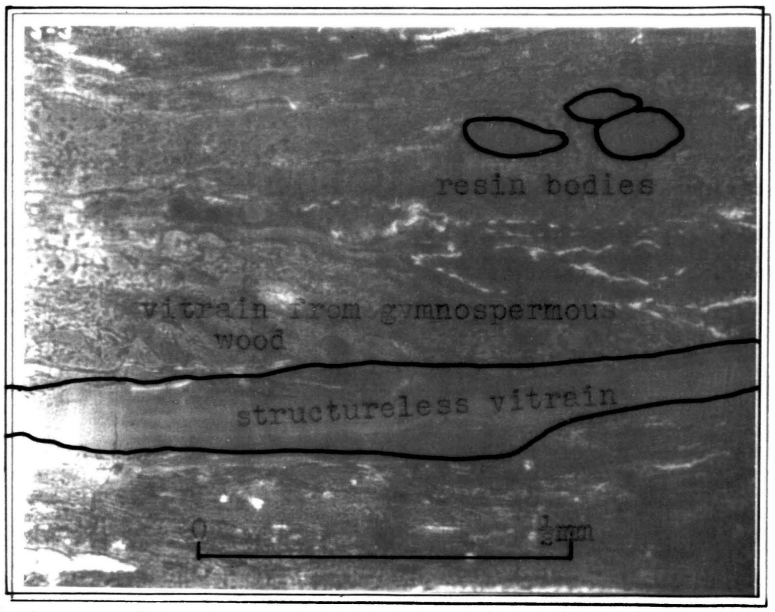


Figure 10. Gymnospermous vitrain with resins.

FIGURE 10

Figure 11. Megaspore(s) in attritus.

FIGURE 11

Along the bottom of the photograph is a band of clear structureless vitrain (called euvitrain). Above this band is a large area of vitrain derived from gymnospermous wood, showing the typical, contorted cell structure. In the top right hand corner are three large oval resin bodies, which are yellowish-brown in thin section. The small white lines in the photograph are probably cuticle fragments. The cuticle is the waxy layer on the surface of a leaf.

Locality No. 2

Table 3 gives the analyses figures obtained from samples of locality no. 2. All the peaks in the ash curve correlate with peaks in the sulphur curve, indicating that pyrite is responsible for the high sulphur values. A value of 2.2 per cent sulphur over a large part of the seam indicates that this is the "background" value for the sulphur concentration. The lower Bevier bench at this locality has sulphur contents higher than this "background" value.

The average crucible swelling number of the seam is about $2\frac{1}{2}$. The cokes produced generally possess a good cellular structure. Samples of high sulphur content have a lower swelling number. The volatile content (ash free basis) ranges from 40 to 44 per cent. Peaks in the ash and sulphur curves are reflected in the volatile (dry basis) curve.

Figure 11 shows a photomicrograph of a megaspore or magaspores in semi-translucent attritus. In thin section the megaspore (s) are seen as bright orange yellow bodies embedded in the darker red attrital matter. The diagonal

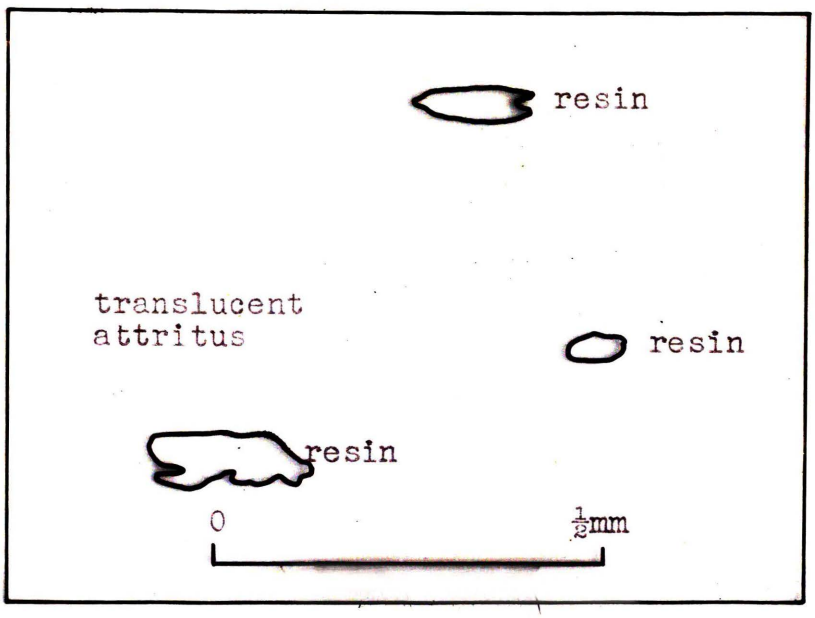


Figure 12. Resin in translucent attritus.

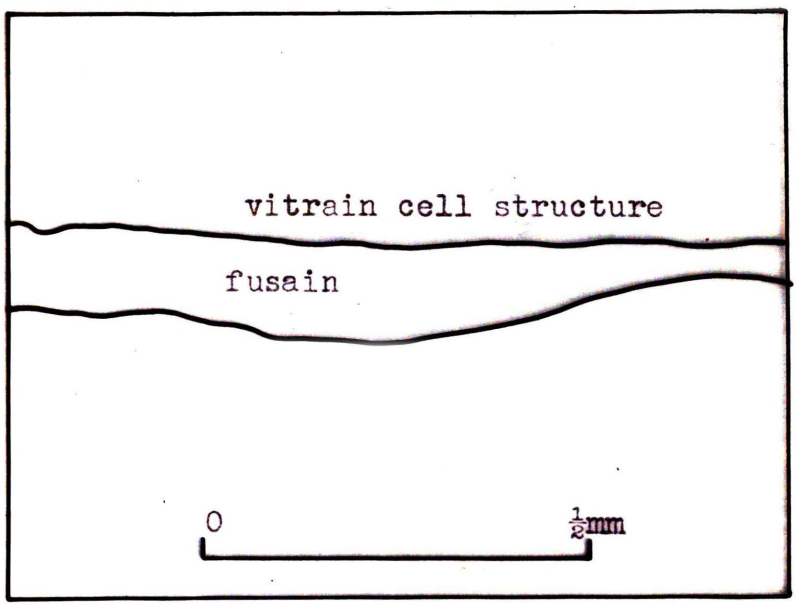


Figure 13. Fusain bands in translucent attritus.

FIGURE 12

FIGURE 13

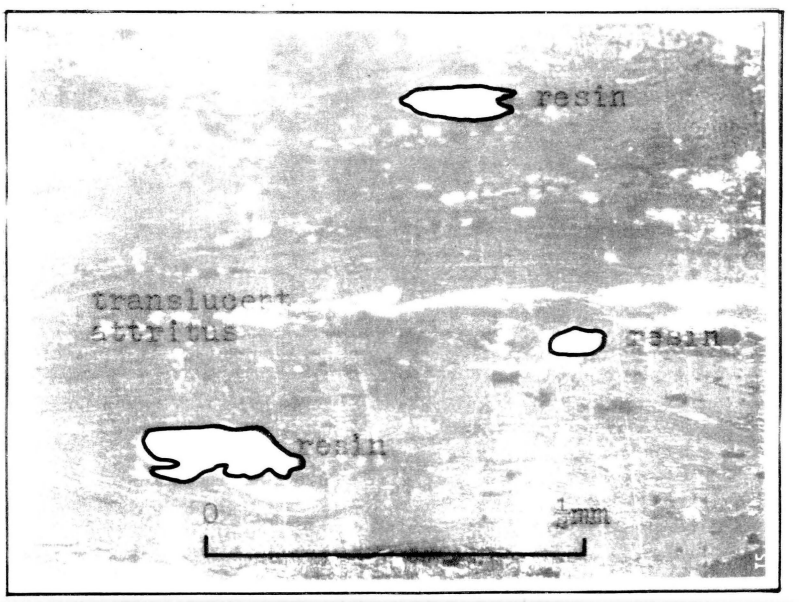


Figure 12. Resin in translucent attritus.

FIGURE 12

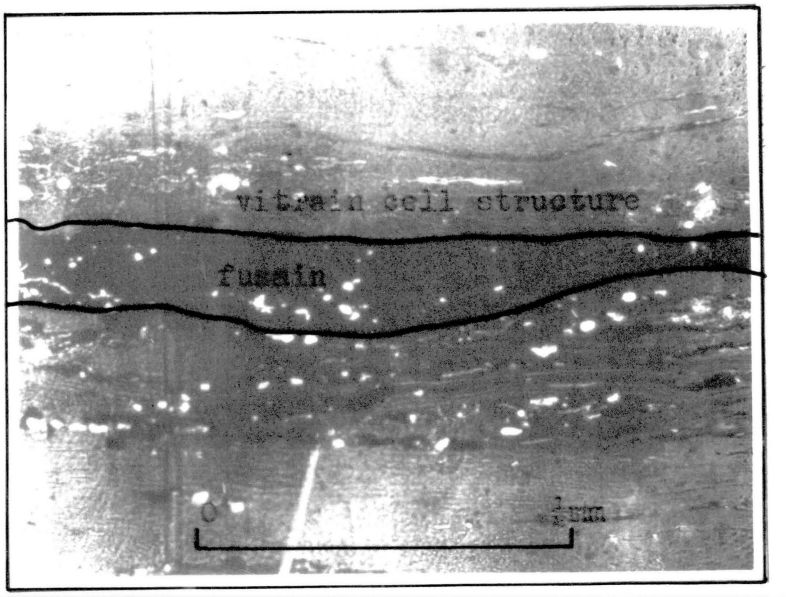


Figure 13. Fusain bands in translucent attritus.

FIGURE 13

white lines are scratches on the surface of the thin section. The coal sample was taken from position 9 in the seam, 21 inches down from the top of the upper bench.

Figure 12 shows a photomicrograph taken of part of a thin section of sample 15. The three large white areas on the photograph are resinous or waxy material, and these appear bright yellow in thin section examinations. The resins were secreted by the coal measure plants in much the same manner that conifers do today. The resinous material is embedded in anthraxylon containing fragments of cuticle and disseminated grains of pyrite. The diagonal thin white lines are scratches on the thin section surface.

Locality No. 3

Table 4 gives the analysis figures obtained from samples taken from locality no. 3. The middle of the seam at this locality has a low ash content. The upper and lower parts of the seam both have high concentrations of ash. Peaks in the ash curve correspond to peaks in the sulphur curve, indicating that pyrite is responsible for the samples with high sulphur content. The "background" sulphur content is about 2.5 per cent. The shale bench at this locality is six inches thick, and consists of alternate layers of thin coal and thin shale. This can be seen from a study of the ash curve for this locality where the high ash samples extend over a wider band in the coal seam.

The uppermost 18 inches of the seam produced coke buttons with swelling numbers of $3\frac{1}{2}$ to 4. The remainder of the seam produced coke buttons with swelling numbers of $1\frac{1}{2}$ to 2. The

ash free volatile matter ranged from 40 to 44 percent in the upper bench of the Bevier seam, and from 37 to 39 per cent in the lower bench. This indicates that the lower bench is of slightly higher rank than the upper bench in this locality. Samples collected from locality No. 2 (only 500 yards away) do not show a higher rank in the lower bench.

An empirical law, proposed by Hilt (Raistrick and Marshall, 1939, p. 238), states that in a vertical succession at any point in the coal field, the rank of coals increase with depth. This is the only locality studied where the two benches obey Hilt's law.

Figure 9 shows a photomicrograph of part of a thin section of sample no. 4. The section shows vitrain with well preserved cell structure, and containing disseminated pyrite. Each of the black areas on the photograph contains a small pyrite grain, which, due to its superior hardness, has remained as a small "topographic" high in the thin section. In the immediate vicinity of each pyrite grain the section is still too thick, producing the black area, which grades into the reds (greys in the photograph) of the translucent vitrain. The small white flecks are holes in the slide.

Figure 13 is a photomicrograph of sample no. 6. The black lens is fusain, showing poor cell structure. One thick layer and several thinner ones are embedded in attrital matter. Beneath the thick fusain band are a few poorly preserved cells of vitrain. Near these cells is a thin white line, which may be either a small spore, or a fragment of cuticle.

SUMMARY

The coals examined from the three localities fall into the "high volatile bituminous (A)" group of the A. S. T. M. classification. Calorific values of the coal analysed ranged from 13,520 to 14,563 B. T. U. per pound (mineral-matter-free basis). Sulphur contents of the channel samples ranged from 3.07 to 6.14 per cent, although some horizons in the seam contained as much as 17 per cent of sulphur. Volatile matter on the ash free basis ranged from 37 to 44 per cent. Crucible swelling numbers ranged from 1 (non-agglomerating) to 4½.

For the coal samples at one locality, correlations were observed between ash content, sulphur content, crucible swelling number, and volatile content. No correlation of these properties with the ingredients of thin sections could be established.

Correlation from one locality to another was impossible using the detailed analysis data. The only features which were constant, over the three localities, were the shale bench which separates the Bevier seam into the upper and lower benches, and the "background" sulphur content (2.2 to 2.5 per cent).

Germanium concentrations ranged from 5 to 100 parts per million of ash.

SUGGESTIONS FOR FURTHER STUDY

(1) More and better thin sections are needed for satisfactory complete this research program.

(2) The spore content of the coal should be investigated, in the interests of long distance correlation, with other coal fields in the Mid West.

(3) Further studies should be made of the oval pyrite grains in the disseminated material, with a view to finding the reason for the poor stability when compared with the pyrite in the cleet.

(4) Further studies should be made of the optical properties of anthraxylon, with reference to the vertical position of the sample in the seam.

(5) Possible substitutes for Goddard's plate powder should be tried.

BIBLIOGRAPHY

British Standards Institution, 1942. British standard methods for the analysis and testing of coal and coke.
British Standards Institution, Publications, No. 1016 pp. 1-74.

Broadhead, G. C., 1873. Macon County. Randolph County.
Missouri Geol. Survey Repts. 1855-1871. pp. 74-110.

Gibson, F. H., and Selvig, W. A., 1944. Rare and uncommon chemical elements in coal.
U. S. Bureau of Mines, Tech. Papers, No. 669, pp. 1-23.

Goldschmidt, V. M., 1930. The presence of germanium in coal and coal products.
Nachr. Gess. Wiss. Gottingen, 1930, pp. 398-399.
(from Chem. Abstracts, Vol. 25, 1931, pp. 3935-3936)

Goldschmidt, V. M., and Peters, C., 1933. The geochemistry of germanium.
Nachr. Gess. Wiss. Gottingen, 1933.
(from Chem. Abstracts, Vol. 28, 1934, Coll. 2648)

Gordon, C. H., 1893. A report on the Bevier sheet.
Missouri Geol. Survey, Vol. 9, pt. 2, pp. 1-75.

Hawn, F., 1855, Mr. Hawn's report.
Missouri Geol. Survey, Second ann. rept., pp. 1-126.

Headlee, A. J. W., and Hunter, R. G., 1951. Germanium in coals of West Virginia.
Geol. and Econ. Surv. of W. Virginia, Rept. of Inv. No. 8, pp. 1-15.

Hinds, H., 1912. The coal deposits of Missouri.

Missouri Bureau of Geol. and Mines, Vol. 11, 2nd series pp. 1-503.

Keyes, M. G., 1925. Making thin sections of rocks.
Am. Jour. Sci. 5th, series, Vol. 10, pp. 538-550.

Lowrey, H. H., 1942. Relation of the physical constitution of coal to its chemical characteristics.
Jour. Geol. Vol. 50, No. 4, pp. 357-384.

Marbut, C. F., 1898. The geology of the Huntsville Quadrangle.
Missouri Geol. Survey, Vol. 12, pt. 2, pp. 311-371.

McCabe, L. C., and Quirke, T. T., 1937. Angle of polarization as an index of coal rank.
Am. Inst. Min. Eng. Trans., Vol. 130, pp. 445-455.

McQueen, H. S., 1943. The geology of the fireclay deposits of Missouri.
Missouri Geol. Survey and Water Resources, Vol. 28, 2nd. series, pp. 1-250.

Morgan, G., and Davies, G. R., 1937. Germanium and gallium in coal ash and flue dust.
Chemistry and Industry, 1937, pp. 717-721.

Powell, A. R., 1921. The analysis of sulphur forms in coal.
U. S. Bureau of Mines Tech. Papers, No. 254, pp. 1-21.

Raistrick, A., and Marshall, C. E., 1939. The nature and origin of coal and coal seams.
English Universities Press Ltd. pp. 1-276.

Ramage, H., 1927. Gallium in flue dust.
Nature, Vol. 119, p. 783.

Searight, W. V., 1949. Coal production, distribution, and consumption in Missouri.

Missouri Geol. Survey, Inf. Circ., No. 3, pp. 1-52.

Sneed, M. C., and Maynard, J. L., 1944. General College Chemistry.

D. van Nostrand Co. Inc. pp. 1-861.

Sprunk, G. C., and Theissen, R., 1935. The relation of microscopic composition of coal to chemical, coking, and by-product properties.

Ind. Eng. Chem., Vol. 27.

Stopes, M. C., 1919. On the four visible ingredients in banded bituminous coal.

Royal Soc., Proc., (B). Vol. 90.

Theissen, R., 1920. Structure in Paleozoic bituminous coals.

U. S. Bureau of Mines, Bull. No. 117, pp. 1-296.

Theissen, R., Sprunk, G. C., and O'Donnel, H. J., 1938. Preparation of thin sections of coal.

U. S. Bureau of Mines, Inf. Circ. No. 7021, pp. 1-8.

Winslow, A., 1891. A preliminary report on the coal deposits of Missouri.

Missouri Geol. Survey, pp. 1-226.

Witham, H., 1832. On the general results of botanical investigation concerning the character of the ancient flora, which by its composition has furnished the material of coal seams.

Brit. Ass. Adv. Sci., 1st and 2nd meeting, report, p. 578.

VITA

Philip John Clarke was born on June 17, 1929 at Sutton-in-Ashfield, Nottinghamshire, Great Britain, the second son of John Dudley and Ivy Clarke. After attending the local grade schools, he entered the Brunts Grammar School in 1939, graduating in 1947. He enrolled at King's College, University of London in October, 1947, and in 1951 graduated with a General B. Sc. Degree in Chemistry, Physics and Geology. After one year of graduate study he was awarded a Diploma in Chemical Engineering.

In September 1952, he accepted a post of Graduate Assistant in the Department of Geology at the Missouri School of Mines and Metallurgy.